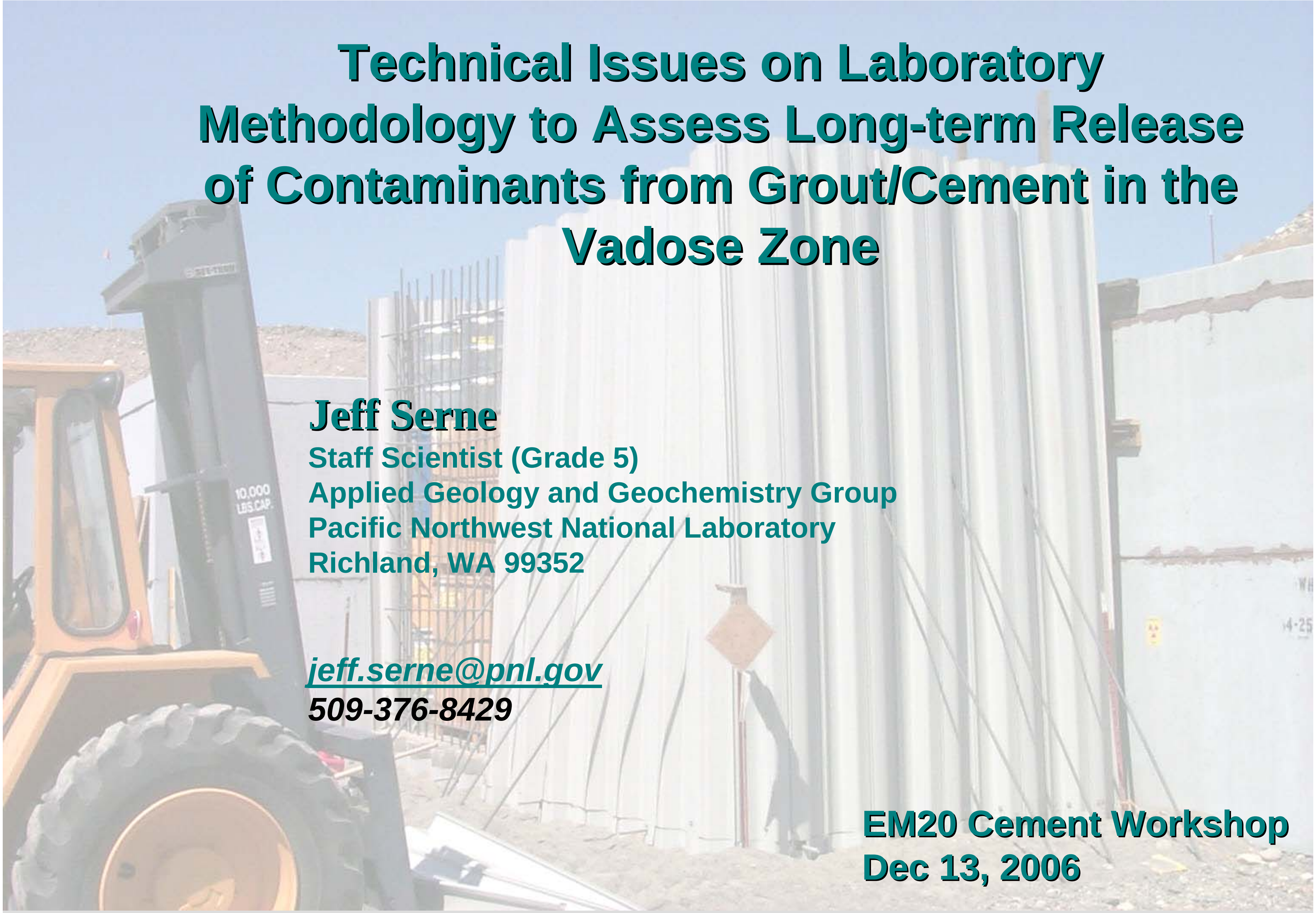

Technical Issues on Laboratory Methodology to Assess Long-term Release of Contaminants from Grout/Cement in the Vadose Zone

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EM20 Cement Workshop
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Topics-Difficulties in Extrapolating Short-term Lab Tests to Long-term Performance Predictions

- Diffusion Experiments using Unsaturated Sediment Half-Cells vs. Water Immersion Tests
  - Reproducible Interface & Water Film Contact
  - “Thin” Sectioning Materials to Measure Diffusion Profile
- Carbonation of Cement/Concrete Specimens to Simulate Aging
  - Super Critical CO_2 vs. Saturated Carbonate Solutions
  - Using Microscopy and Solid Phase Characterization Instruments
  - Do Observed Micro-cracks Form During Sample Prep?
- Measuring Reducing Capacity of Grouts
  - Angus & Glasser (1985) vs Lee & Batchelor (2003) differ by factor of 20 for blast furnace slag

Hanford Motivation: Concrete Encasement of LLW

Soil-Soil Half Cell Diffusion

Soil Half Cell - Cold

4.13 cm ID x L ~20.7 cm

Mass Water Content: 4, 7,15 %wt

Bulk Density: 1.4 – 1.6 g/cm^3

Soil Half Cell - Spiked

4.13 cm ID x L ~20.4 cm

Mass Water Content: 4, 7, 15%wt

Bulk Density: 1.3- 1.5 g/cm^3

Spike: I^- A_0 ~607 ppm, $^{99}Tc(VII)$ A_0 ~13 nCi/g

Diffusion Time, Temp.

64,169, >365 days @ ~25 ^{O}C

Concrete-Soil Half Cell Diffusion

Soil Half Cells

4.13 cm ID x L 20.4 cm

Mass Water Content: 4,7, 15%wt

Bulk Density: 1.4 g/cm^3

Concrete Half Cells

4.13 cm ID x L 4.2 cm

Portland cement	**25%**
Sand	**50%**
Class F fly ash	**5%**
Steel fibers	**5%**
Water	**15%**

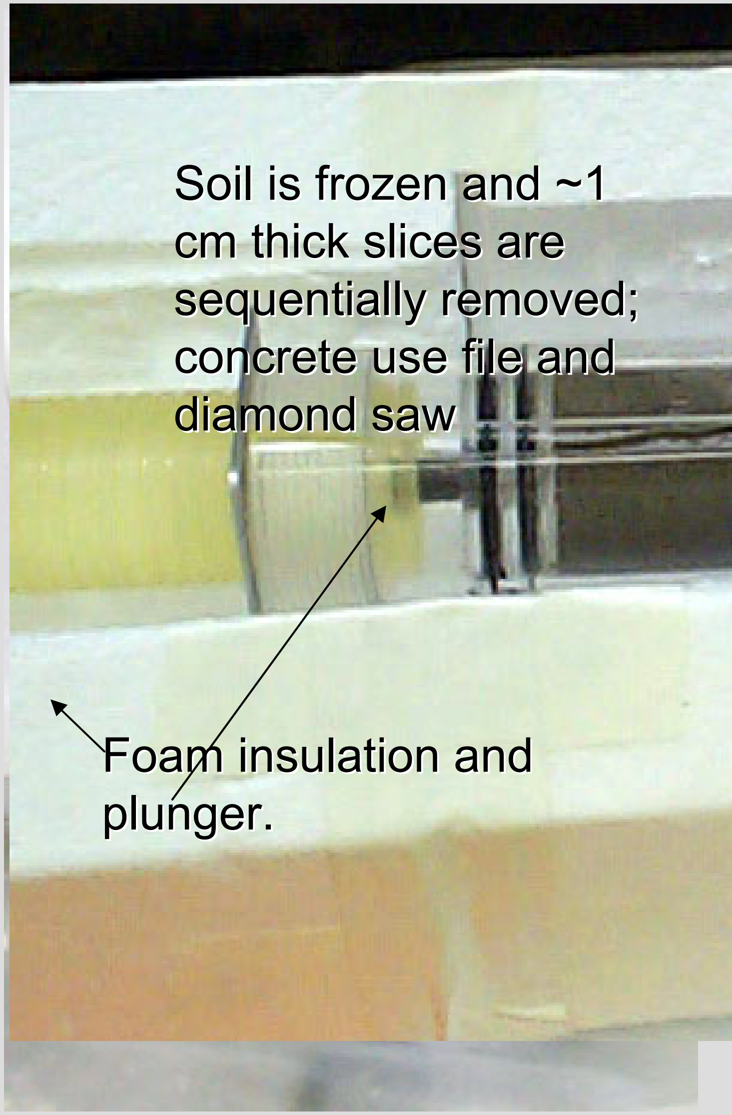
Spike 460 ppm stable I^-

~30 nCi/kg ^{99}Tc or ~400 ppm stable Re(VII)

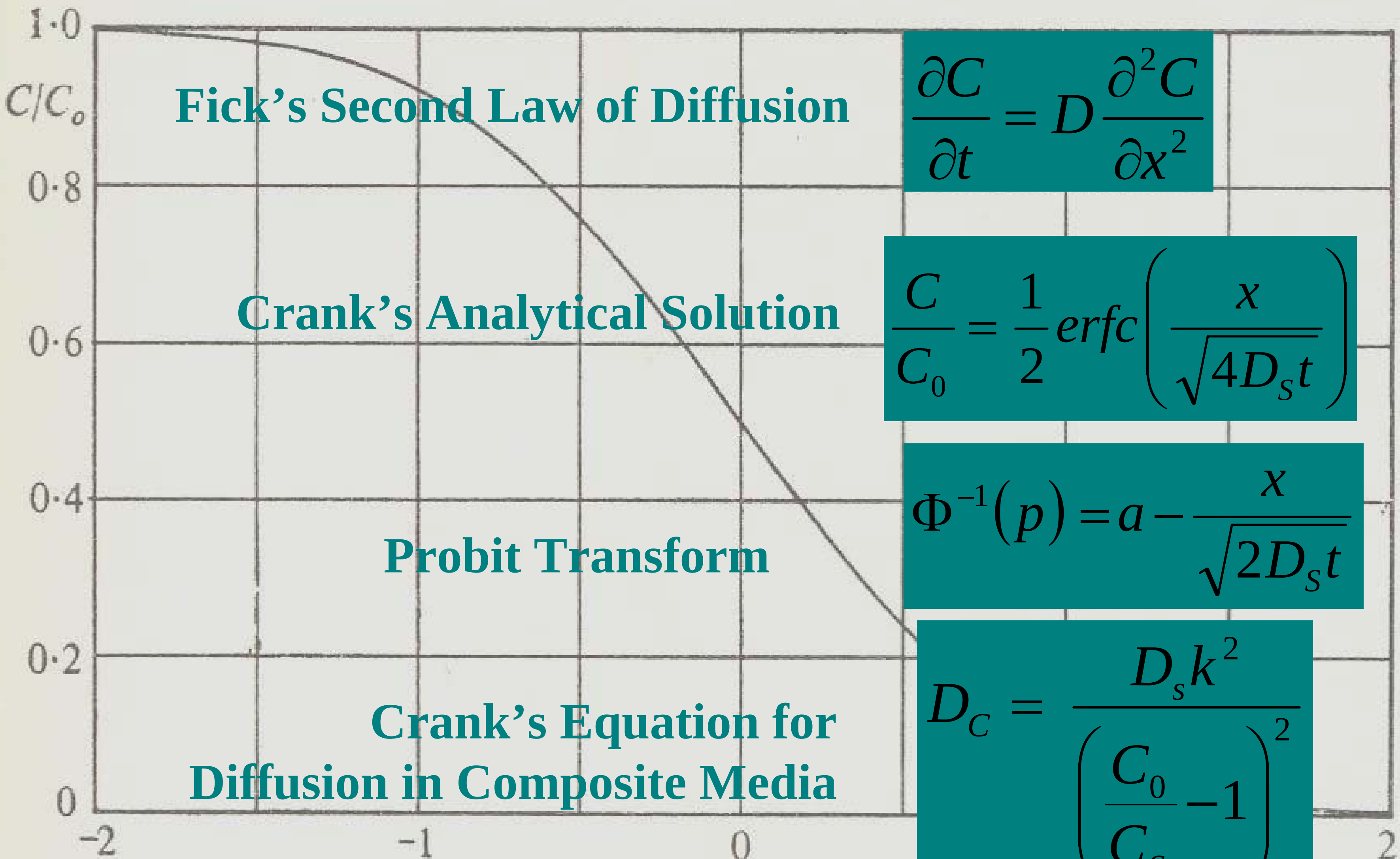
Diffusion Time, Temp.

64,169, >365 days @ ~25 ^{o}C

Sampling Diffusion Cells



Diffusivity Calculations



Fick's Second Law of Diffusion

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

Crank's Analytical Solution

$$\frac{C}{C_0} = \frac{1}{2}erfc\left(\frac{x}{\sqrt{4D_S t}}\right)$$

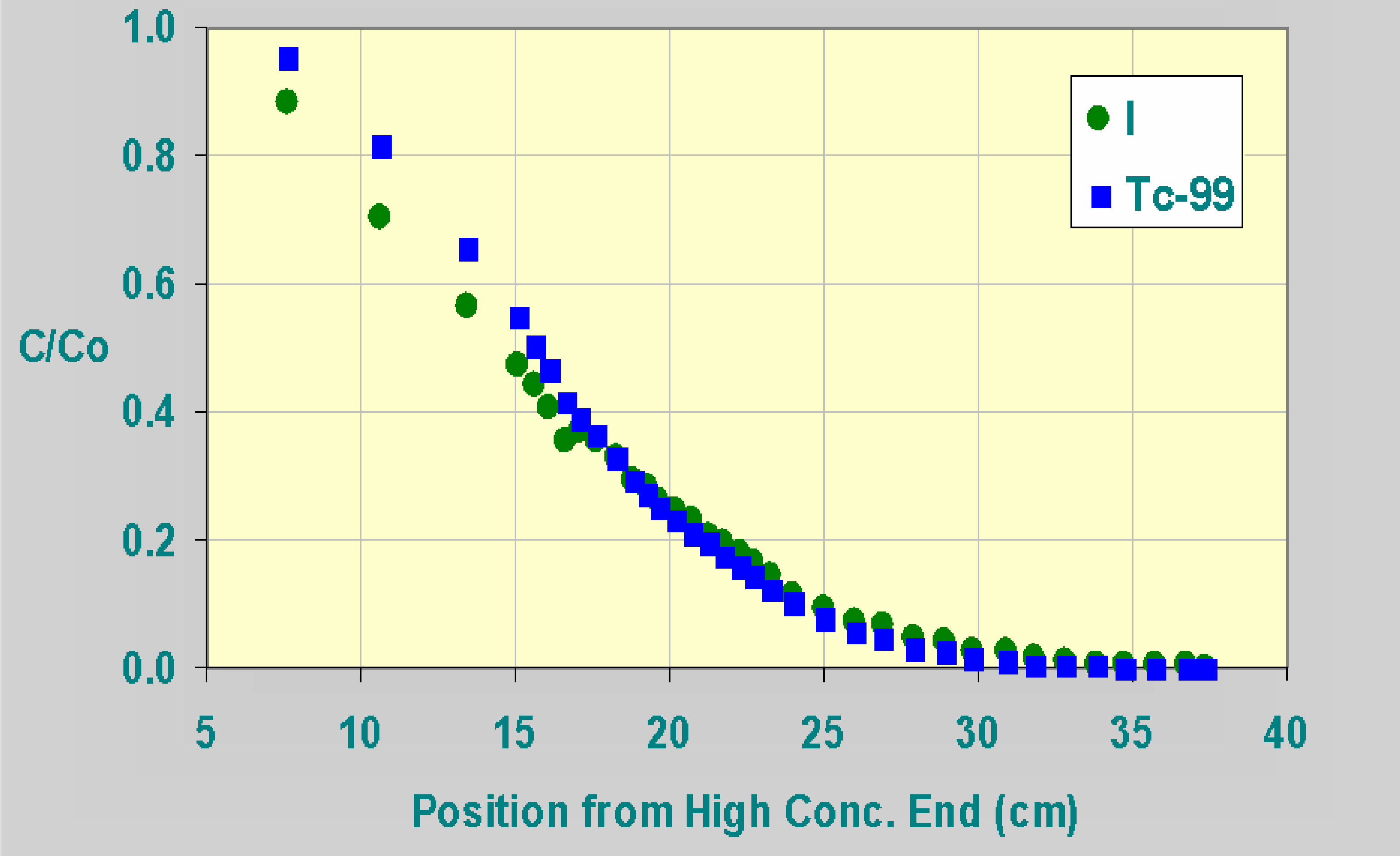
Probit Transform

$$\Phi^{-1}(p) = a - \frac{x}{\sqrt{2D_S t}}$$

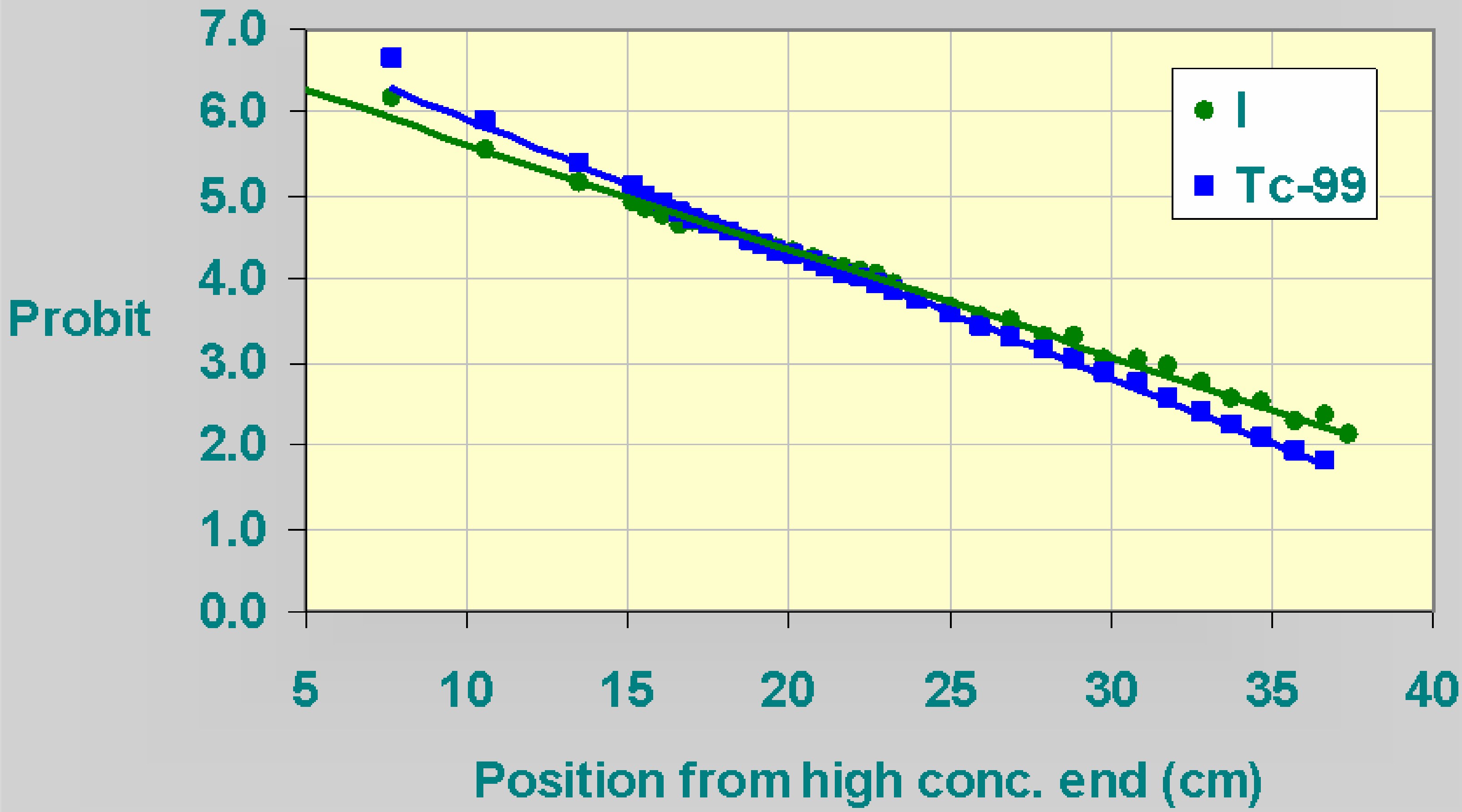
Crank's Equation for Diffusion in Composite Media

$$D_C = \frac{D_s k^2}{\left(\frac{C_0}{C_S} - 1\right)^2}$$

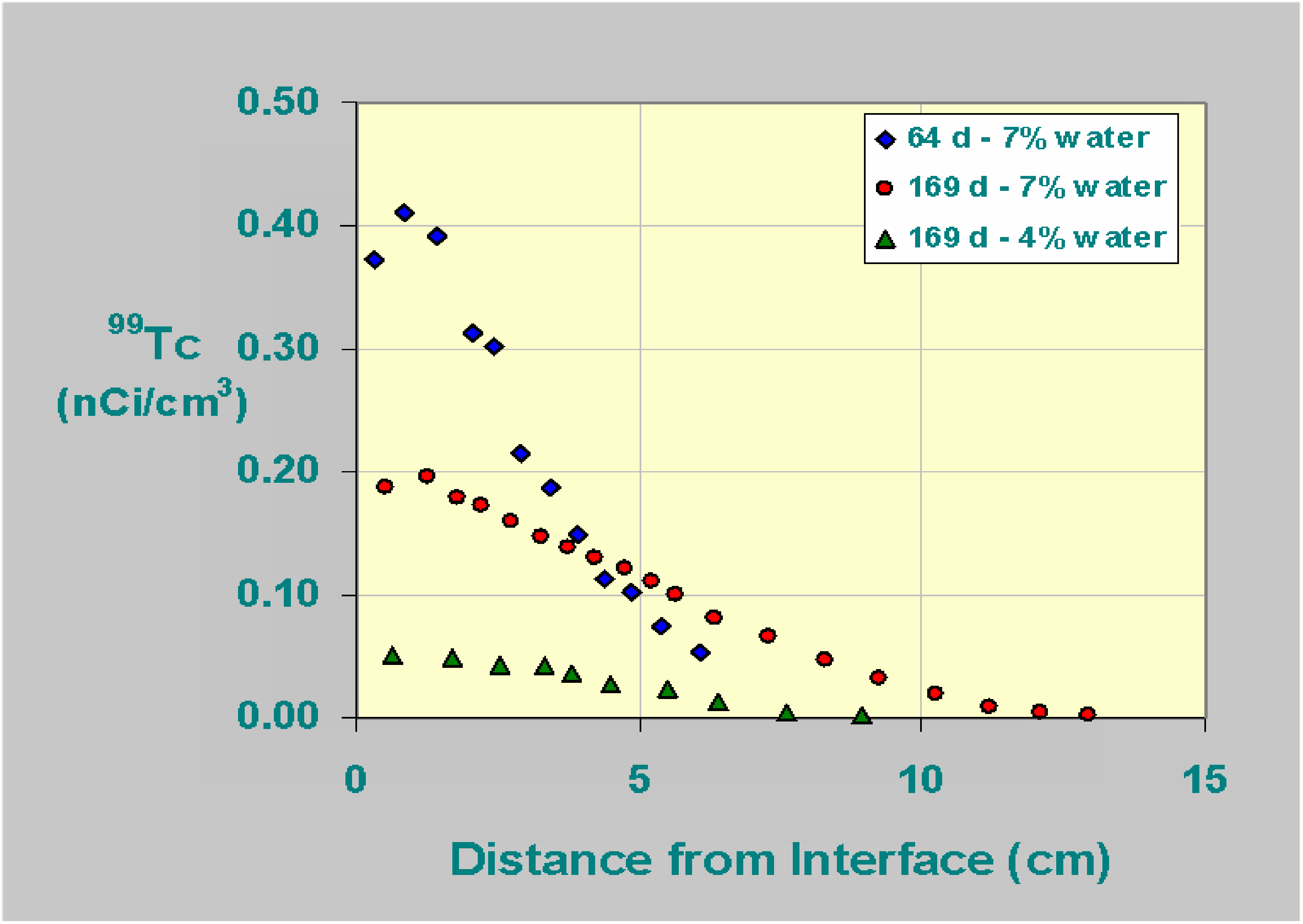
Diffusion Profile - Soil/Soil Half Cell



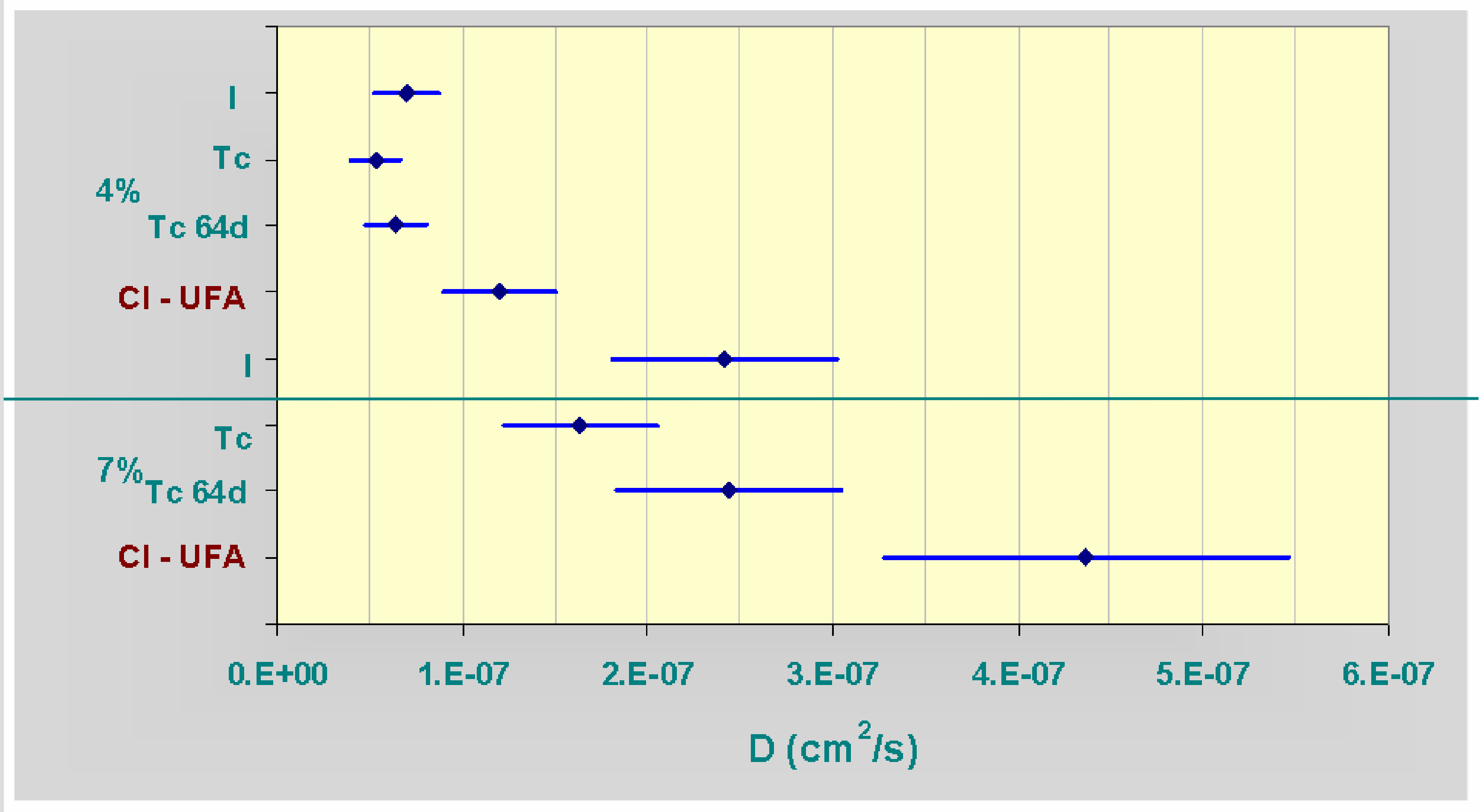
Soil/Soil Half Cell - Probit Plot



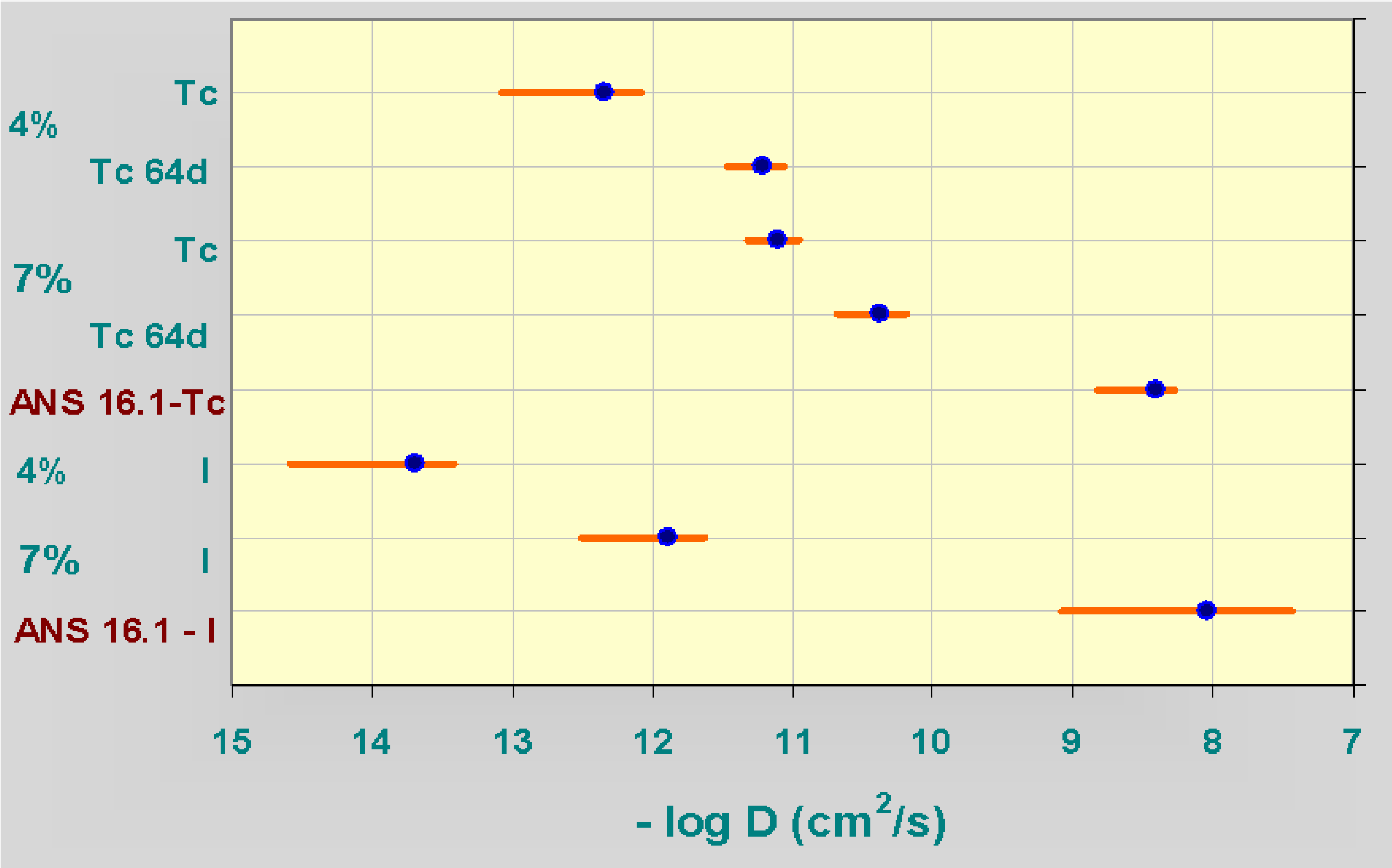
^{99}Tc Diffusion Profile - Concrete/Soil Half Cell



^{99}Tc and I Diffusivity - Unsaturated Soils



^{99}Tc and I Diffusivity - Concrete



Synopsis

Soil diffusivity of Iodine and ^{99}Tc in unsaturated Soil

^{99}Tc and I diffuse ~ 4 X slower at lower water content (~5 x 10^{-8} cm^2/s @ 4% and ~2 x 10^{-7} cm^2/s @ 7%)

Diffusivity of these ions are ~50% of Cl diffusivity observed in a number of soils at similar water contents. Soil-Soil Half Cell Lab results seem reasonable.

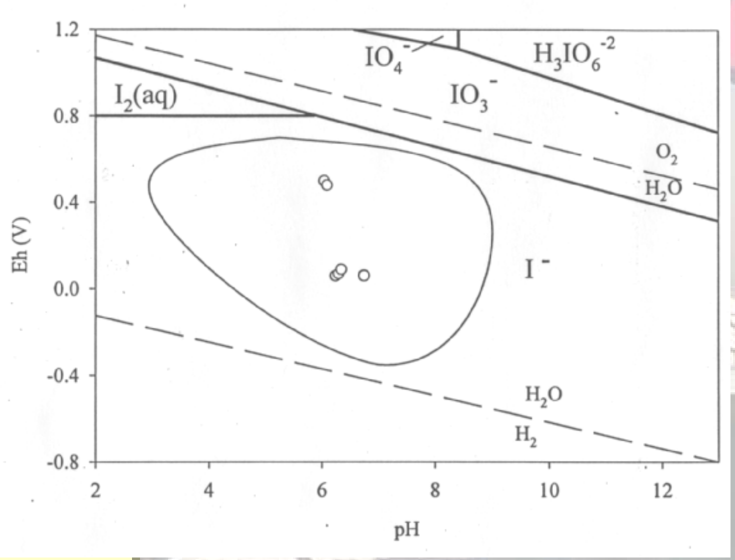
So maybe Concrete-Soil Half Cell results are too?

Synopsis

Diffusivity of I and ^{99}Tc in Waste Encasement concrete

Ions diffuse 1 – 2 orders of magnitude faster at higher moisture content—7 wt% vs 4 wt%

I diffuses 1–3 orders of magnitude more slowly than ^{99}Tc
I: ~2×10^{-14} – 1×10^{-12} cm^2/s
^{99}Tc: ~2×10^{-13} – 5×10^{-11} cm^2/s)



Diffusivity of I and ^{99}Tc: Unsat Half Cell Experiments 4 – 6 orders of magnitude lower than values calculated from ANS 16.1 leach tests. Which test is realistic?

Carbonation

- Used super critical CO_2
  - When carbonated monoliths ANS16.1 leached--- higher than expected release was found--- suspected micro-cracking
  - Cracking may have been artifact of releasing pressure at end of carbonation---Is cracking realistic.
  - Wide-spread calcite rind but surprised at small depth of penetration.
  - No visible or petrographic microscope surface cracking but resolution is >8 to10 µm. Used ASTM C856.

- Now using saturated sodium bicarbonate and two weeks constant soak

- SEM-EDS shows more and longer micro-cracks in SCF-carbonated specimens; but all specimens show cracking
  - Average width is 1 micron
  - Separation cracks common around aggregate and fly ash
  - Cracks are not filled
  - **Despite sample prep crack possibilities, carbonated specimens have more than not carbonated ones**

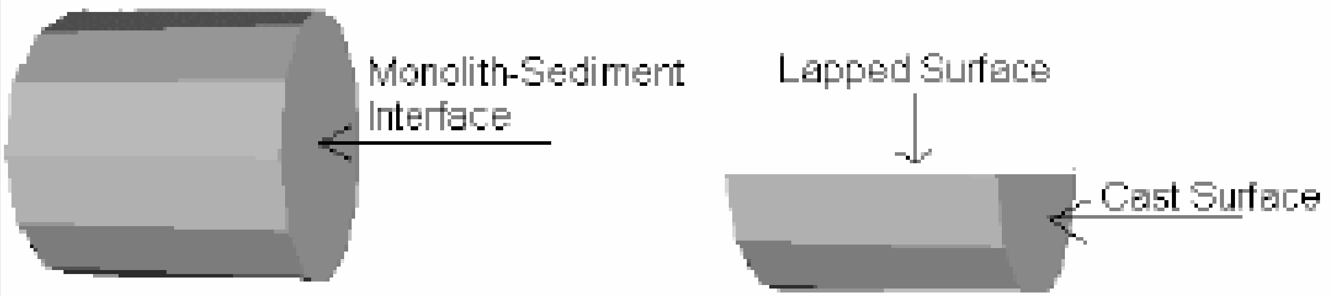
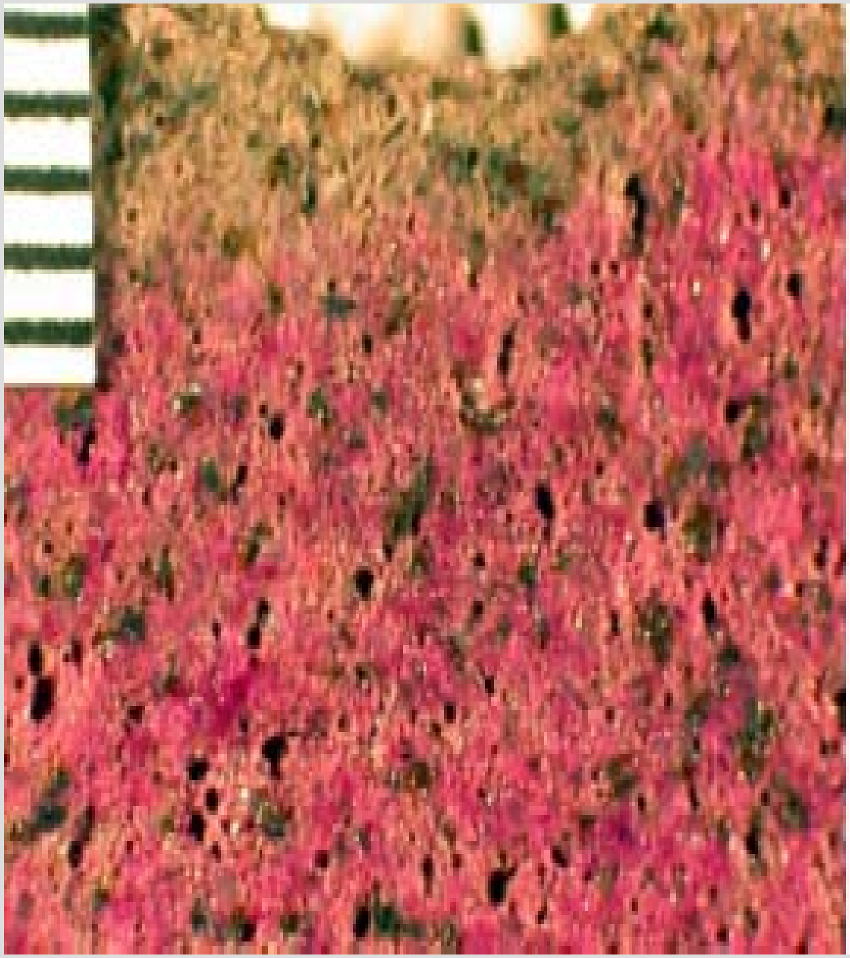


Figure 3-6. Schematic illustrating concrete treatment and surface designations for petrographic analysis.

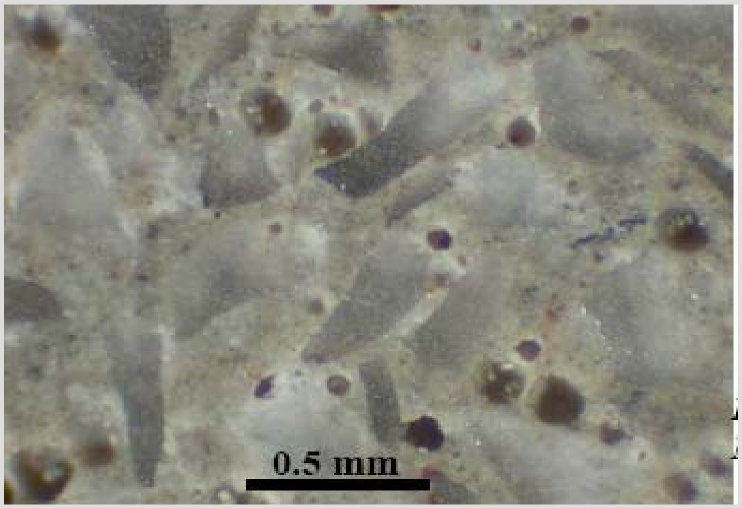
Depth of Carbonation-used SCF

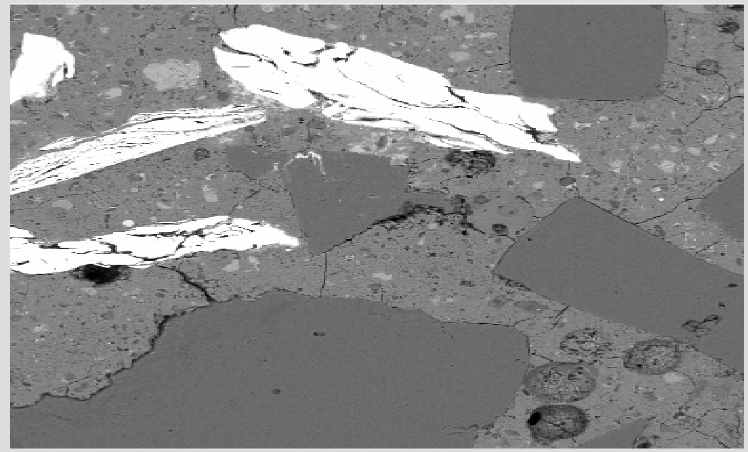
(L) No Carb Concrete next to 4 wt% sed=1 to 2 mm

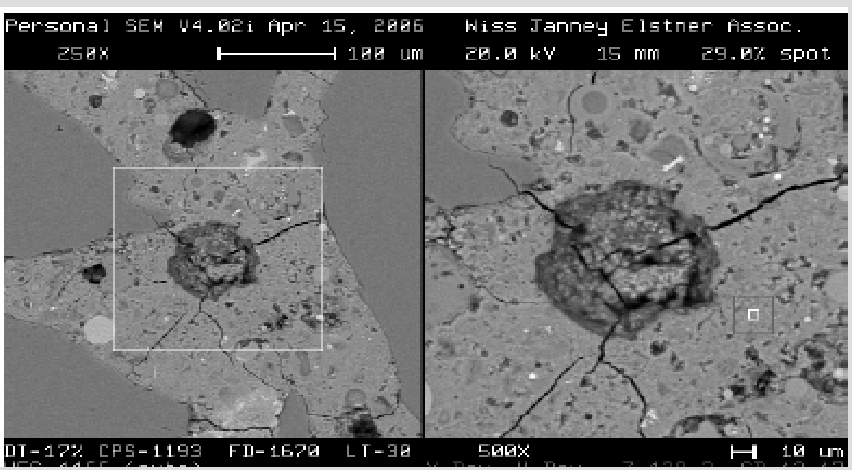
(R) Carb Concrete next to 7wt% sed= 4 to 8 mm



Petrographic and SEM of SCF-Carbonated Concrete (UL= low mag Pet UR=100X BSE LL= 250&500X LR=500&5000X)







Carbonation Synopsis

- Does Micro-cracking Occur because of Acceleration or Sample Preparation?
- Rates of Carbonation
  - Hanford building concrete (outside walls above ground)
    - 57 yr old--- carbonation to 48-53 mm; cracks common (0.8 to 0.9 mm/y)
    - 28 yr old--- carbonation to 2-8 mm; no cracks (0.07 to 0.28 mm/y)
    - 14 yr old--- carbonation t0 1-10 mm; no cracks (0.07 to 0.71 mm/y)
  - Super Critical CO_2 (2.2 mL water and CO2 at 35°C and 8.4 MPa)
    - 1 day carbonated to 8-10 mm; micro-cracks (1 µm wide) observed in SEM
  - Saturated sodium bicarbonate soln (soak 2 weeks)
    - Data not available yet
- Need more data & data from other’s attempts

Poising and Reductive Capacity of Dry Blend Materials

- Angus and Glasser
  - 1 g of oven dry solid in contact with 50 mL 0.05M ceric[Ce(IV)] ammonium sulfate in 2M sulfuric acid
  - Stir 1 hr; back titrate reduced Ce (III) with 0.1M ferrous ammonium sulfate until Pt electrode-calomel ref reaches 1.057 volt (ave of formal E^0 for Fe(III)/Fe(II) and Ce(IV)/Ce(III)
  - Yields moles e^- per g of solid (or moles Ce(IV) reduced/g)
- Lee and Batchelor
  - Done in anoxic chamber (95% Nitrogen-5% hydrogen)
  - 1 g of dry solid in contact with 10 mL of variable M Cr(VI) solution in 0.01M sodium bicarbonate; keep slurry pH at 7; stir for 4 days @ 22°C
  - Add 0.142 g sodium sulfate (makes slurry 0.1M sulfate) to desorb chromate bound to solids; centrifuge; filter supernate
  - Measure initial and final Cr(VI); calculate equiv.[chromate consumed] per g

Measurement of Blast Furnace Slag used in SRS Saltstone

- Angus and Glasser method gives value 20X larger than Lee and Batchelor method (work done by Dan Kaplan)
- Kaplan got same results on other materials as authors (thus Δ is in methods not materials)
- Has impact of length of time reducing conditions are maintained in long-term PA as O_2 diffuses back in---Δ20X [Saltstone PA used Angus and Glasser value]
- Serne believes real world environment closer to Lee and Batchelor (neutral pH, cement additives don’t dissolve just evolve/age) thus impacts Saltstone PA calculations

Conclusions---Lots of Questions But No Answers

- Are "water immersion" leach tests appropriate for concrete/cement waste forms in shallow land burial environments?
- Can one overcome method difficulties in using unsaturated half-cell test methodologies and what data reduction equations are correct?
- How do you accelerate the ageing of specimens and then characterize the solids without introducing artifacts ("accelerated stress" micro-cracks during carbonation, drying, mounting for microscopy, vacuum coating etc)?
- Do micro-cracks that are ~1 uM in diameter and not very long or randomly connected really matter for mass transport?
- How do you accurately measure the "reducing" capacity of cement and common additives?

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